

# **Refinery Products Volatile Organic Compounds Emissions Estimator (RP-VOC)**

---

*User Manual and Technical Documentation*

**Energy Systems Division  
Argonne National Laboratory**

**About Argonne National Laboratory**

Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see [www.anl.gov](http://www.anl.gov).

**DOCUMENT AVAILABILITY**

**Online Access:** U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free at OSTI.GOV (<http://www.osti.gov/>), a service of the US Dept. of Energy's Office of Scientific and Technical Information.

**Reports not in digital format may be purchased by the public from the****National Technical Information Service (NTIS):**

U.S. Department of Commerce  
National Technical Information Service  
5301 Shawnee Rd  
Alexandria, VA 22312  
**[www.ntis.gov](http://www.ntis.gov)**  
Phone: (800) 553-NTIS (6847) or (703) 605-6000  
Fax: (703) 605-6900  
Email: **[orders@ntis.gov](mailto:orders@ntis.gov)**

**Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):**

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
**[www.osti.gov](http://www.osti.gov)**  
Phone: (865) 576-8401  
Fax: (865) 576-5728  
Email: **[reports@osti.gov](mailto:reports@osti.gov)**

**Disclaimer**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

# Refinery Products Volatile Organic Compounds Emissions Estimator (RP-VOC)

---

*User Manual and Technical Documentation*

Energy Systems Division, Argonne National Laboratory

prepared by

John Beath<sup>1</sup>, Paula Vosmus<sup>1</sup>, Rachel Kazanski<sup>1</sup>, Sarah Backes<sup>1</sup>, Brandie Sebastian<sup>1</sup>, Greg Zaines<sup>2</sup>, Troy Hawkins<sup>2</sup>

<sup>1</sup>John Beath Environmental, Beaumont, Texas

<sup>2</sup>Systems Assessment Center, Energy Systems Division, Argonne National Laboratory, Lemont, Illinois

December 2020

## **Introduction**

The estimation of well-to-distributor volatile organic compound (VOC) emissions resulting from the extraction of crude oil in an oilfield, transportation to a crude oil terminal upstream of the refinery, operation of the refinery, and subsequent pipeline and product distribution has previously been approached as a top-down industry-wide average; RP-VOC performs its core calculations using a “from-the-ground-up” approach. By taking this approach, the tool results can be used for the supply network of a single refinery, or to generalize the average performance of all refineries.

VOC emissions contribute to ozone formation in combination with nitrous oxide (NO<sub>x</sub>) compounds which can potentially present regional health concerns for sensitized exposed individuals in some settings. Understanding what aspects of the system contribute the most is the first step at prioritizing plans for future reductions.

This tool consists of two modules to estimate VOC emissions from individual piping components and storage tanks, which are the largest emission sources of VOC within a refinery.

The storage tank emissions module relies on EPA’s AP-42 Compilation of Air Emissions Factors (most recently updated in January 2019). It is the first publicly available storage tank emissions tool to be released since EPA’s TANKS Emissions Estimation Software Version 4.09D (which EPA labeled as outdated in 2006). The new tool goes beyond TANKS 4.09D by connecting an entire set of tanks throughout the supply chain and configuring them based on the specified refinery size.

The piping components emissions tool consolidates methods recommended by EPA<sup>1</sup> and production source count information developed by the Texas Commission on Environmental Quality (TCEQ)<sup>2</sup>. While published tables provide variations on these emissions factors for various situations<sup>3</sup>, to our knowledge this is the first such publicly available tool to estimate VOC emissions based on a set of source counts.

The piping tool consolidates these source counts to cover the well site, crude storage tank areas and terminals, the refinery, the downstream distribution terminal, and all associated pipelines.

The combination of tank and leaking piping component tools covers all of the life cycle stages up to distribution terminals, and downstream emissions for transportation fuels are already within the scope of EPA’s MOVES model. Results can be connected to petroleum production elements within the Argonne National Laboratory (ANL)’s Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) life cycle model to estimate VOC emissions from oil processing throughout the supply, refining, and distribution chain.

These new granular estimates of VOC emissions enhance the quality and accuracy of GREET estimates.

Analysis of data obtained from RP-VOC calculations highlights the significant impacts from the use of small tanks at the wellhead where gathering lines are not in place, as well as the potential implications of leak detection and repair (LDAR) programs in the upstream stages of the supply chain. Both impacts are typically larger than corresponding refinery impacts that have been the subject of increasingly restrictive control measures over time.

## **Tank Emissions Tool**

### **Required Data Inputs**

The tank tool estimates VOC emissions from tanks for a national average case, in addition to estimating emissions from a case based on refinery configuration data inputs. These variables are described below.

Key to the attractiveness of a model is the required input data and whether that data is available. While a user seeking to model a specific facility may have ample data available, a significant challenge in making this tool average across the industry was in the development of representative data that was from publicly available sources.

Much of the data used by GREET1 is obtained from the US Energy Information Agency (EIA), and this data is not made available facility-by-facility; instead, it is aggregated at the national or Petroleum Administration for Defense District (PADD) level.

### *Crude Speciation*

In order to accurately determine storage tank emissions, the vapor pressure of the stored product and its vapor molecular weight must be specified. To provide default national average data, values for these key parameters needed to be developed and provided. As part of its GHG baseline development efforts, the National Environmental Energy Laboratory (NETL) develops an average of crudes run by PADD. The last version of this published was for 2014. This data was used for the construction of a national average crude blend. Public assay data was located for each of the major contributors to the crude blend and this was used to develop a chemical speciation for each crude contributor, and ultimately for the blend.

The resulting blend (and for reference each of its contributors) were subject to a flash calculation using chemical-specific Antoine Coefficients which were obtained from EPA's AP-42 (Table 7.1-1). This flash calculation resulted in the speciation of the vapor which, in turn set the estimate of the mixture's vapor pressure and molecular weight.

### *Refined Product Speciation*

In a similar fashion, published data on speciation for stored refinery intermediate products and final products were located from various publications. This data was also subject to a flash calculation using the Antoine Coefficients of the mixture components to determine vapor characteristics.

### *Meteorological Data*

AP-42 provides maximum and minimum temperature by month and for the year, as well as wind speed data for a long list of US cities. This data was updated by EPA in 2018. The data tables for this have been included in the tank tool. The user can select the city for crude extraction and for the refinery. To provide conservative results, the city chosen was on the gulf coast, Baton Rouge, Louisiana. A more geographic average location that is in the meteorological data tables would be Oklahoma, City, OK; but no refineries are located there.

The tank tool has been modified from a comprehensive version such that it does not calculate on a monthly basis; instead, emissions for a representative average month are multiplied by twelve to get emissions for the year. This change was made to streamline the data input process and because it is likely that users seeking only national average results would not have this specific data.

### *Tank Physical Characteristics*

The number and size of tanks at a refinery will vary but is a strong function of the facility design crude rate. Crude, intermediate and product tank capacity are typically specified based on the desired buffer time, e.g., seven to fourteen days of operation at design rate. The tank tool design basis was a refinery in Louisiana for which a detailed permit application was available online. This refinery was used to set the initial sizing and to benchmark the emissions results obtained by using its specific consideration and assumed local crude slate. Tank sizing was held constant and the number of tanks is adjusted as a linear function of the specified crude rate.

The type of control for the tank depends on the stored material vapor pressure. EPA and state regulation will require the use of floating roof tanks for refineries (selection of internal floating roof or external floating roof is left to facility preference). Lower vapor pressure materials can be stored in fixed roof tanks, though some refiners gain more flexibility by storing some heavier materials in spare floating roof tanks.

Upstream crude oil tanks at the wellhead are much smaller than those at refineries and as such can qualify for an exclusion from the floating roof requirement if small enough (e.g., less than 500 barrels).

### *Tank Throughput*

Once the crude rate is specified, the refinery throughput is set based on the assumption that rate is attained as an average every calendar day. There is an important caveat here. AP-42 emissions calculations were revised in 2018 to reflect the fact that not all movement through a tank results in emissions.

For a floating roof tank, working loss emissions only result from the evaporation of the film exposed on the inside of the tank shell when the roof is moving downwards.

For a fixed roof tank, working loss emissions occur when the tank is gaining liquid because this displaces air that is emitted via conservation vents at the top of the tank.

Experience has shown that if emissions are only calculated when floating roofs are falling, or when fixed roof tanks have a level that is rising, will be perhaps 30% less than if true throughput had been used for these calculations. This analysis would require actual tank operating data, so the model sticks with the more conservative use of all the tank throughput. If a user has actual withdrawal and addition data, the default values in the tool can be overridden.

The throughputs of refinery product and intermediate tanks were developed using the University of Calgary's PRELIM refinery flowsheet model. The results of that analysis are stored in a tab called "Case Study." The user is cautioned not to modify this data. The results are quite helpful because they show how yields would compare for various crude types as well as the custom blend that is the national average.

### **Operating Instructions**

The model input cells are highlighted as light yellow. Changing other cells may erase formulas or default configuration data. The user is cautioned to proceed carefully if changes are made, recognizing that it is always possible to start over with a fresh downloaded version of the model.

#### *Specifying Key Case Study Parameters for Tanks ("[Case\\_Evaluation](#)" tab)*

The case tool provided on this tab has two features – it sets the model input, and it can be used to store the results from various case studies. On initial use, it is set with default parameters. This portion of the tank tool operates using a key "trick" that leverages the fact that *Microsoft Excel* stores both the current value in the cell, and its previous value. Though this previous value can't be exposed directly, it can be leveraged. This is accomplished by a circular reference made part of a logical "IF" formula. In each of the case study results columns, the value is only changed if the case number in the input column matches the case number of the results column. If not, any changes in the input column don't impact the case results columns that don't have the same case number.

In the “User Input” column, the crude rate is specified (100,000 BPD as a default). This is also where the crude type is selected from the library of crudes where publicly available data has been provided. The user can also specify the well location, the crude oil distribution terminal location, and the refinery location.

There are also two other important specifications that are inputs in this tab: (1) the percent of the wells that are not serviced by gathering lines; and (2) whether the refinery has a coker or not.

To store multiple cases, change the case number in the User Input Column and the results will be delivered to the corresponding column. **Importantly, note that other tables in the tool will only correspond to the current values in the User Input Column.**

#### *Specifying Refinery Tanks (“Full\_Tank\_Summary” tab)*

The tank tool provides a table of default crude oil, intermediate and final product storage tanks for the refinery (upper-left corner of this workbook tab). As a default, the tank diameters and tank count are specified based on the model refinery and the specified crude rate. User override columns are provided so that a user could develop an inventory where specific data is available.

To the right of this table is a breakdown of key details for each tank service. This table is called “Refinery Tank Input/Output Table.” The model supports three crude types but is set to handle the national average as a default. Though a user could add additional tank types the model does not automate this process currently; that is, they would need to be wired to various places in the model. The user can change the service of any of the tank types using the “Tank Contents” row.

This table also provides an opportunity to alter the temperature for heavy service tanks that may require heating in winter (e.g., residual oil). The tool is not currently configured to address asphalt tank emissions calculations that are specified by a separate set of equations in AP-42. Note that the physical property library that supports heated tanks only has values up to 300 degrees F (see “Chemical” tab for physical properties). The tank throughputs can be altered on the Product Yields tab.

#### *Specifying Other Tanks – Non-Refinery (“CrudeOil\_Tank\_Summary” tab)*

The network of tanks needed at the wellhead and both upstream of the refinery and downstream (in terminals) is largely determined based on the specified crude rate of the refinery.



Default throughputs are determined mathematically from the crude rate. Therefore, throughput changes (other than to adjust for withdrawal versus throughput) are not recommended.

The number of tanks in service is defined based on the percent of tanks with gathering lines (set in tab discussed above). In the “Well Platform Operations” table the user can override the default assumption about how much time the pipelines may be available.

In the table at the right labeled “VOC Calculator – Offsite Storage Tank Emissions” the user can adjust the default tank diameter, tank height, throughput and tank temperature (if heated).

#### *Specifying Refinery Product Yields (“**Product Yields**” tab)*

The national average crude slate (a hybrid of the top crude oil types based on their relative proportion) was introduced into the PRELIM flowsheet model and resulting intermediate and product stream rates were estimated based on volume balances and various reactor yield formulas contained within the model. To simplify the VOC tank tool, the hydrorefinery configuration was elected with a mild hydrocracker. This eliminates the production of #6 Fuel Oil as a product, instead converting those heavy oil barrels into lighter products.

The “CaseStudy” tab contains PRELIM model results for various crude types that are available in Prelim and were a component of the hybrid used to produce the national average crude supply.

Though the results for various crude assay PRELIM case studies are stored in the “CaseStudy” tab, these have not been wired to the model, nor is the model connected to PRELIM directly (results were transferred via a set of formulas that drive the User Input column and require that the crude type be manually selected in the PRELIM model).

To overcome this limitation, the “Product Yields” tab has an override column that allows the user to specify any rate in barrels per day for any of the products or intermediates.

Though any values can be specified via override, a useful result set should be based on a sum of products that is near the 100,000 BPD crude charge rate. For example, if more than average gasoline is specified, this could be offset by specifying less diesel. The assumption is that all produced product must initially be stored in a tank prior to loading or transmission via pipeline to a downstream distribution terminal.

The model assumes that marketing terminal product tanks are identical to those in the refinery for products.

For refinery intermediate streams, the most conservative assumption would be that each produced intermediate is stored in a tank before it is charged to a downstream unit. Not every refinery is operated this way, and certainly not for every intermediate produced by each refinery unit. To simplify the VOC calculator, it was assumed that only those intermediate

storage tanks that the model refinery had would be selected. One key variable is whether alkylate is stored separately or routed to a mix tank where various other gasoline blend stocks may also be stored. The PRELIM case did not predict the production of alkylate based on the national average crude slate, so no intermediate storage for alkylate is provided as default.

The sum of refinery intermediates on a barrel per day basis is less than the crude rate, supporting the premise that some of the intermediate products are routed directly to downstream units without storage.

#### *Refinery Loading Product Input (“**GREET NonTool**” tab)*

Tank emissions results are aggregated in various overall summary pages. This summary shows the results from the LDAR tool (see discussion in the next section), as well as other activities. Loading emissions are approximated in this tab based on the amount of gasoline product produced. Override percentages are accepted on this tab if the user seeks to vary the results from the default assumed percentages for marine and tank car/truck loading. The assumption would be that the balance of the gasoline product is transferred via pipeline and there would be no emissions from this (beyond LDAR).

#### *Connecting the LDAR Results to the Tank VOC Calculator (“**VOC\_Summary**” tab)*

The LDAR tool is a separate workbook but its results are presented in summary tables within the tank tool. This tab contains links that collect the results from the LDAR workbook and present them in the “VOC Emissions” table under “Case 1 Refinery.” The results for the National Average are also wired via links to the LDAR workbook so that changes made to it are delivered to this tab. Users are cautioned that generally making changes to the National Average case are not advised as there is no way to restore to default values except by backtracking, or doing a fresh download.

## **Leaking Piping Component Emissions Tool**

### **Equipment Configuration**

This tool (referred to as the “LDAR tool”) operates under a simple premise: that leaking pipeline component emissions can be calculated by multiplying component counts by an emissions factor. The emissions factor is adjusted based on the extent to which an effort is made to control emissions by various leak detection and repair (LDAR) programs.

Component counts are provided based on the type of process unit for a refinery and on a per-tank basis in tank farms.

These control programs specify periodic monitoring using a photoionization device, and for leaks in excess of a specified threshold, required maintenance actions to reduce the measured leak emissions below the leak threshold. These repairs include tightening seal packings, equipment overhaul, and in extreme cases, equipment replacement. These piping components consist of valves, flanges, pumps, open-ended lines, drains and other less numerous piping elements. More innovative monitoring techniques are being tested and are allowed in some cases (e.g., infrared video cameras), but the current factors do not provide estimates for those approaches.

Emissions estimates are divided between light and heavy volatile organic compounds (VOC) because typically light VOC components will have periodic monitoring while heavy components will not. Heavy component leak rates will have lower emissions due to lower volatility, but this will be partially offset by the increase in emissions resulting by the fact that there is no control applied. Note that some programs do require repair of heavy component leaks when incidentally identified (e.g., because there is dripping liquid).

#### *Well Head Yield Data (“[Summary\\_Ref\\_Custom](#)” tab)*

The user can overwrite the default values for well production and tanks per well, but these values are not linked to the tank tool, so unless changed there as well, these overrides would not produce consistent results for piping leak emissions and tank emissions. There is also the possibility of changing the crude rate for this workbook, but once again it is better to hold the same value for both the VOC tool and the LDAR tool.

This tab also accepts input as to what type of Leak Detection and Repair (LDAR) program is used to control emissions. It is possible to specify no control program, but if so, emissions will be significantly higher. The program for the wellhead, crude oil gathering tank farm, crude distribution terminal and downstream marketing terminal are all specified in the table called “Upstream/Downstream Fugitive Emissions - Emissions Factors.” ***This tab also presents the overall results for the custom refinery and its associated upstream and downstream associated equipment.***

#### *Refinery Component Data (“[Ref\\_Custom](#)” tab)*

Each refinery process unit has a default number of piping components based on EPA average operating data collected in a refinery survey in 2011. Separate tables of component counts by unit are included for large and small refineries, either with or without a coker. Thus, the user can specify if the refinery is large or small (<50,000 bpd) and whether or not the refinery has a coker, and the component count will adjust accordingly.

The LDAR tool provides the user with an opportunity to override the counts by specifying multiple units for each of the types in the listing. The default value is based on the national average number of units of each type in a refinery, but a user may wish to override this by conservatively specifying a second unit. This tab is wired so that the appropriate source counts are delivered to it based on the large/small and coker/no coker elections.

The table called “Refinery Fugitive Emissions - Emissions Factors” allows the user to select the control program for the refinery (e.g., 28 MID). Control efficiencies for the various programs are provided in the tab called “Reduction Factors” based on guidance developed by the Texas Commission on Environmental Quality (TCEQ).

### **Leak Factors**

Data underlying this configuration cannot be modified via overrides.

Leak factors are hard-wired based on the equipment type, whether the source is in heavy or light VOC service, and whether the component is at a refinery or elsewhere. Leak factors are provided in the tab called “OG\_Factors” but modified by a control factor from the “ReductionFactors” tab.

### **Transferring Values to VOC Tank Tool**

See explanation in the Tank Tool section.

## **References**

1. *U.S. Environmental Protection Agency TANKS Emissions Estimation Software, Version 4.09D*
2. *AP 42, Fifth Edition Compilation of Air Pollutant Emissions Factors, Volume 1: Stationary Point and Area Sources, Chapter 7, Liquid Storage Tanks.*
3. *U.S. Energy Information Administration - Petroleum & Other Liquids - Refinery Capacity Report. Website: [eia.gov/petroleum/refinerycapacity/](http://eia.gov/petroleum/refinerycapacity/)*
4. *Emission Estimation Protocol for Petroleum Refineries, Version 3, April 2015. Section 2-Equipment Leaks, Page 2-16, Table 2-5.*
5. *Emission Estimation Protocol for Petroleum Refineries, Version 3, April 2015. Section 2-Equipment Leaks, Page 2-15, Table 2-4.*
6. *Characterization of Oil and Gas Production Equipment and Develop a Methodology to Estimate Statewide Emissions, Nov. 2010.*
7. *Air Permit Technical Guidance for Chemical Sources, Fugitive Guidance, APDG 6422, TCEQ, June 2018.*
8. *Emission Estimation Protocol for Petroleum Refineries, May 2011*



## **Energy Systems Division**

Argonne National Laboratory  
9700 South Cass Avenue, Bldg. 362  
Argonne, IL 60439

[www.anl.gov](http://www.anl.gov)



Argonne National Laboratory is a U.S. Department of Energy  
laboratory managed by UChicago Argonne, LLC